Quantitative Analysis of Hydrogen in High-Hydrogen-Content Material of Magnesium Hydride via Laser-Induced Breakdown Spectroscopy

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Quantitative Analysis of Hydrogen in High-Hydrogen-Content Material of Magnesium Hydride via Laser-Induced Breakdown Spectroscopy

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Abstract

An analytical approach that can rapidly determine a wide range of hydrogen concentration in solid-state materials has been recently demanded to contribute to hydrogen economy. This study presents a method for estimating hydrogen concentrations ranging from 0.2 to 7.6 mass% *via* laser-induced breakdown spectroscopy (LIBS) in a few seconds, with an improvement in the upper limit of determination (7.6 mass%) by approximately 1.3 times compared with a previous work (5.7 mass%). This extension of the determinable concentration range was achieved by measuring the emission intensity at 656.28 nm from the sample in a helium atmosphere at 3000 Pa under focused laser irradiation and by reducing the water residues in both the sample and gas line of LIBS system. The as-determined hydrogen concentrations in magnesium hydride (MgH_2) samples agreed well with those estimated through inert gas fusion/gas chromatography. The calibration curve for LIBS analysis was acquired by measuring the emission intensity at 656.28 nm of standard Mg/MgH_2 mixtures containing various hydrogen concentrations (0, 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 7.6 mass%). Results indicated that the proposed LIBS-based method is applicable to the rapid quantitative analysis of hydrogen in hydrogen-containing material of MgH_2.

1. INTRODUCTION

The demand for the quantitative analysis of hydrogen in solid-state substances has recently grown owing to the increasing studies on materials related to hydrogen production, transportation, storage, and utilization (e.g., fuel cells, hydrogen storage materials, and structural materials for hydrogen transportation) for the realization of an environmentally friendly society. Several analytical techniques are currently applied for this purpose, including thermal desorption spectroscopy,[1] inert gas or vacuum fusion/gas chromatography,[2,3] secondary-ion mass spectrometry (SIMS),[4,5] and glow discharge optical emission spectrometry (GD-OES).[6] However, their application areas are limited; for example, SIMS is limited to trace analysis (ppb–ppm), whereas GD-OES can perform only a rough concentration determination. Moreover, all these methods are not rapid. Therefore, an analytical technique that can rapidly determine the hydrogen content in a wide concentration range is desirable for practical applications.

Laser-induced breakdown spectroscopy (LIBS) is one of the most promising methods to satisfy the above-mentioned requirements, since its measurement duration is only a few seconds. This technique acquires the optical spectrum emitted by atoms evaporated from a sample as a result of irradiation with a high-power-density pulsed laser. Several studies have investigated its application to the quantitative analysis of hydrogen.[7-19] Kurniawan et al. have aggressively tackled this topic, reporting that among air, nitrogen, and helium atmospheres, a reduced helium atmosphere provides the highest enhancement in the hydrogen emission line (H I 656.28 nm), and approximately 10 ppm of hydrogen in zircaloy pipe can be detected *via* LIBS.[8] Afterward, for the same material, they observed a linear relationship between hydrogen emission intensity and concentration at hydrogen concentrations below 960 ppm.[9] Furthermore, this upper limit was increased to 4300 ppm (0.43 mass%) by using the intensity ratio between H I 656.28 nm and zirconium emission line (Zr I 655.0 nm), which was selected as an internal standard emission line, and irradiating defocused laser on the zircaloy samples.[10] Rapin et al. evaluated water content in geological materials, such as basalts, calcium and magnesium sulfates, opals, and apatites, using H I 656.28 nm emission line in Martian atmosphere (~800 Pa).[18] They found a single linear calibration curve applicable to all these materials after normalizing the hydrogen line by a carbon or oxygen line emitted from the ambient gas. By using the calibration curve, they estimated the water content up to 51%, which corresponded to 5.7 mass% of hydrogen. For the further widespread use of LIBS for

hydrogen analysis, the determinable concentration range must be extended toward the upper limit; moreover, the use of a focused laser is favorable to the application of LIBS for two- and three-dimensional analyses.

The present study aimed to develop a method that can quantify hydrogen in materials with high hydrogen concentrations (above 5.7 mass%) *via* LIBS with a focused pulsed laser. We selected magnesium hydride (MgH_2) as the target sample since it contains a relatively high concentration of hydrogen (7.6 mass%) and is one of the most promising hydrogen storage materials.[20-22] To the best of our knowledge, this study is the first one attempting to determine hydrogen concentrations up to 7.6 mass%.

2. EXPERIMENTAL

First, we measured the emission intensities of standard mixtures of magnesium (purity: 99.9%, grain size: below 140 μm, Mitsuwa Chemicals Co. Ltd., Osaka, Japan) and MgH_2 (grain size: 100 μm, FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) powders, pressed in pellets at 500 MPa, to build the calibration curve. The hydrogen concentration in the MgH_2 powder was 7.6 mass%, which was confirmed *via* an inert gas fusion/gas chromatograph equipped with a thermal conductivity detector (EMGA-821, HORIBA, Ltd., Kyoto, Japan). The standard mixtures contained the following hydrogen concentrations: 0, 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 7.6 mass%. Those with 0 and 7.6 mass% hydrogen were obtained by using only the Mg and MgH_2 powder, respectively, whereas the other ones were prepared by mixing appropriate amounts of the two powders with an agate motor. Their concentrations except for the standard samples with 0 and 7.6 mass% hydrogen were determined from the weight of the Mg and MgH_2 powder. The standard samples were stored in a desiccator containing silica gel for more than 3 days before the LIBS measurements to remove the adsorbed water.

Then, to determine the hydrogen concentration in actual samples *via* LIBS, a series of MgH_2 pellets with different hydrogen concentrations were prepared by heating the MgH_2 powder at 350 °C under an argon flow with a flow rate of 200 mL min^{-1} for 2, 3, 4, and 6 h, followed by pressing at 500 MPa. We also measured the hydrogen contents of these samples through inert gas fusion/gas chromatography to confirm the validity of the LIBS results.

The LIBS measurements were performed using the custom LIBS system presented in Figure 1 and described in detail in previous reports.[23-25] In brief, the samples were placed in a chamber, which enabled the atmosphere control by introducing gas and the connection to a rotary pump. A moisture trap (GL Sciences Inc., Tokyo, Japan) was attached to the gas line between the chamber and the gas cylinder to remove the water molecules from the introduced helium or argon gas, unlike in the previous LIBS system. A quality-switched neodymium-doped yttrium aluminum garnet laser (LOTIS TII, LS-2137) with a wavelength of 532 nm was irradiated on the samples; the energy at the samples and duration of this pulsed laser were 30 mJ/pulse and 16–18 ns, respectively. The energy was adjusted using an attenuator which was placed along the optical path. The laser was focused on the samples by a plano-convex lens with a focal length of 150 mm, and the spot size of the laser pulse was 250 μm.[23-25] The light emitted from the generated plasma was dispersed and detected using a Czerny–Turner spectrograph (MS 7504i, SOL Instruments Ltd., Minsk, Belarus) and an intensified charge-coupled device (ICCD) detector (DH334T-18F-03, Andor Technology Ltd., Belfast, UK); the ICCD detector gate was triggered by each laser pulse, and the relative delay was controlled by a digital delay generator integrated into the ICCD detector. For each measurement, a spectrum was acquired for each laser pulse individually, and the pulsed laser was irradiated twice in sequence on the same point. This measurement was repeated for a total of 10 different location points. The distance among each measurement point was above 1 mm. Table 1 presents the LIBS measurement conditions, which were selected because they provided the highest H I 656.28 nm emission intensities from the standard samples. We performed LIBS measurements under reduced helium and argon atmospheres. The reduced helium environment was selected, because as mentioned in the Introduction, it is suitable for the LIBS analysis of hydrogen.[8] As regards the reduced argon atmosphere, although it is appropriate for LIBS measurements on several elements, such as magnesium, aluminum, silicon, chromium, iron, and zinc, compared with the other inert gas, air, and nitrogen atmospheres,[26-33] there are no reports on its use for the analysis of hydrogen.

Table 1. Operating conditions for the laser-induced breakdown spectroscopy measurements.

Chamber		Intensified charge-coupled device detector	
Atmosphere	Pressure [Pa]	Gate width [μs]	Relative delay [ns]
Helium	3000	500	100
Argon	100	1000	50

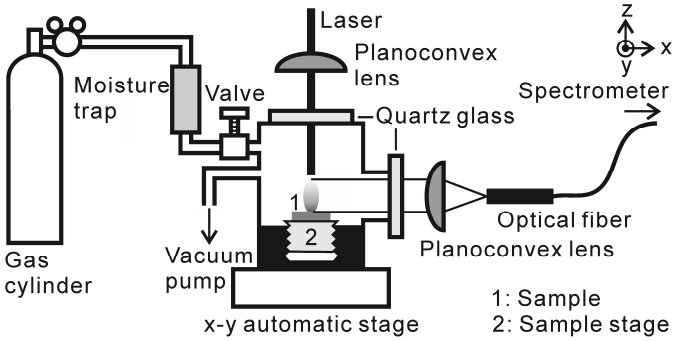

Figure 1. Schematic illustration of the laser-induced breakdown spectroscopy system.

3. RESULTS AND DISCUSSION

3.1 Calibration

Figure 2 shows the LIBS spectra of a standard sample with the hydrogen concentration of 3 mass% under reduced helium and argon atmospheres; under both conditions, the pulsed laser was irradiated twice in sequence on the same point. The spectra obtained with the second irradiation were used for building the calibration curve to reduce the effect of the water impurities from the samples. The pulsed laser was not irradiated three times and more in sequence because intensities of H I 656.28 nm line were almost constant after the second irradiation. An intense H I 656.28 nm line, which originates from a non-resonance transition of hydrogen ($3d\ ^2D_{3/2,5/2}$, 12.088 eV → $2p\ ^2P_{1/2,3/2}$, 10.199 eV),[34] was observed in the spectra of all samples except that with 0 mass%. Figure 3 and Table 2 presents the obtained straight-line relationship between the intensity of H I 656.28 nm line and the hydrogen concentration under both atmospheres. These results indicate that the water molecules adsorbed on the samples were effectively removed via the storage in the desiccator. In general, the LIBS calibration curves negatively deviate from a straight line at high concentrations due to the self-absorption effect, that is, the reabsorption of the emitted radiation by the atoms in their ground-state energy levels and located in the colder external part of the plasma, which may deteriorate the analytical precision.[35] However, the straight-line calibration curve observed in the present study suggests that our LIBS measurements were free from the self-absorption effect, ensuring a precise quantification of hydrogen concentrations below 7.6 mass% under the adopted conditions.

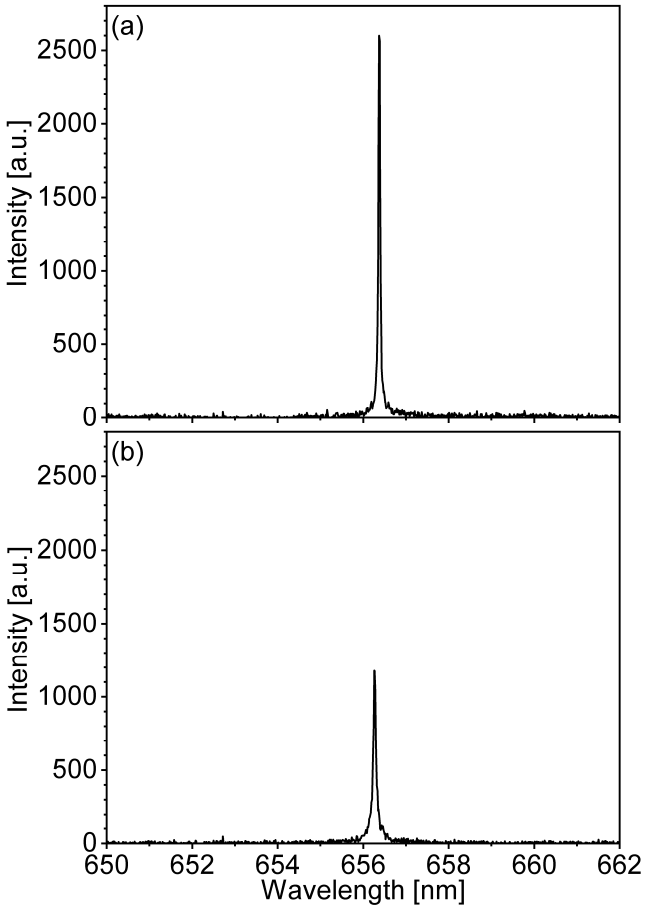

Figure 2. Laser-induced breakdown spectroscopy spectra of a standard sample with a hydrogen concentration of 3.0 mass%, measured under reduced (a) helium (3000 Pa) and (b) argon (100 Pa) atmospheres.

Table 2. Intensity, standard deviation (SD), and relative standard deviation (RSD) of the hydrogen emission line (H I 656.28 nm line) for standard samples under reduced helium (3000 Pa) and argon (100 Pa) atmospheres. Each emission intensity value reported in the table is the average of 10 values.

Atmosphere	Helium (3000 Pa)			Argon (100 Pa)		
Hydrogen concentration (mass%)	Intensity [a.u.]	SD [a.u.]	RSD [%]	Intensity [a.u.]	SD [a.u.]	RSD [%]
0	207	15	7.0	241	25	10.4
0.2	413	72	17.3	409	32	7.8
0.5	820	120	14.7	530	67	12.7
1.0	1073	185	17.2	614	61	9.9
2.0	1748	303	17.3	978	184	18.8
3.0	2597	397	15.3	1145	169	14.7
4.0	3845	288	7.5	1598	297	18.6
5.0	4166	281	6.7	1552	199	12.8
7.6	5709	228	4.0	2232	139	6.2

Previous work reported higher LIBS emission intensities for several elements under reduced argon rather than reduced helium.[26-33] However, in the present experiment, the intensity of H I 656.28 nm line measured under 100 Pa argon was less than half that under 3000 Pa helium (Figure 2). As a result, the slope of the calibration curve for the argon atmosphere was approximately one-third smaller than that for the helium atmosphere (Figure 3). This outcome is related to the excitation energies of the metastable states of the argon and helium atoms; the argon metastable states are $3s^2 3p^5(^2P_{3/2})4s$ (11.548 eV) and $3s^2 3p^5(^2P_{1/2})4s$ (11.723 eV), whereas the helium meta

stable state corresponds to 1s2s (19.820 eV).[32] The metastable state of helium is responsible for the hydrogen excitation *via* an energy transfer mechanism involving the following Penning-like chemi-ionization process;[36,37]

$$He^* + H \rightarrow He + H^+ + e \qquad (1).$$

The resulting hydrogen ion (1s $^2S_{1/2}$, 13.606 eV)[34] is rapidly recombined with an electron, and then, a high-lying excited hydrogen atom, whose energy is just below 13.606 eV, is de-excited to lower excited states, such as 3d $^2D_{3/2,5/2}$ (12.088 eV).[34] Helium atoms in the metastable state (19.820 eV) can provide enough energy for hydrogen atoms in the ground state (0 eV) to be ionized (13.606 eV), whereas argon atoms in the metastable states (11.548 and 11.723 eV) cannot. Thus, hydrogen atoms in the 3d excited state, which is the upper energy level of the H I 656.28 nm line, in the plasma generated under helium atmosphere are more abundant than that under argon atmosphere. This explains the larger emission intensity and calibration curve slope obtained under reduced helium atmosphere. We conclude that these were the reasons for which the previous studies adopted reduced helium atmospheres for the LIBS measurement of hydrogen rather than reduced argon atmospheres.

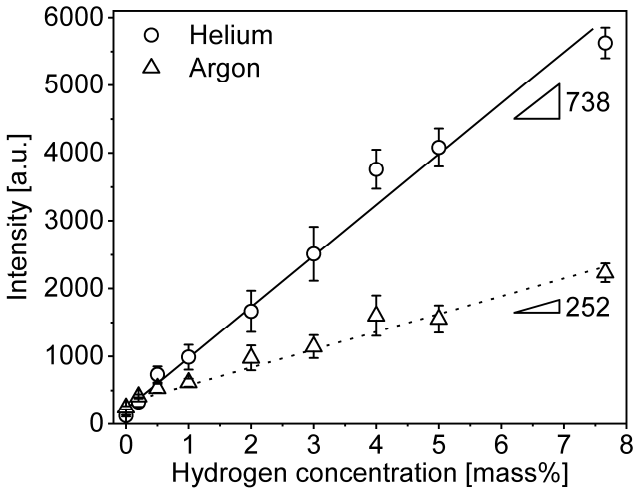

Figure 3. Calibration curve based on the intensity of the hydrogen emission line (H 656.28 nm line) measured under reduced helium (3000 Pa) and argon (100 Pa) atmospheres. The error bars represent one standard deviation.

For the successive experiment on actual hydrogen-containing samples, we used the calibration curve derived under the reduced helium atmosphere because of its larger slope. Its lower limit of quantification (LOQ) was estimated as follows:

$$LOQ = 10\,\sigma_{BG} / a \qquad (2),$$

where σ_{BG} denotes the standard deviation for the sample containing 0 mass% of hydrogen and a denotes the slope of the calibration curve.[38,39] We calculated a LOQ of 0.20 mass%, implying a determinable hydrogen concentration range of 0.2–7.6 mass%, which is sufficient to quantify hydrogen content of hydrogen storage alloys.

However, a LOQ improvement could further extend the applicability of the proposed LIBS-based method to solid-state materials with hydrogen concentrations of the order of ppm, such as steel and titanium alloys. Hence, we developed the following approach to improve this LOQ. The LIBS spectrum of the standard sample containing 0 mass% of hydrogen, which represented our blank, still showed H I 656.28 nm line (Figure 4(a)); thus, identifying the origin of this signal from the blank sample was crucial for the LOQ improvement. The emission intensity increased when removing the moisture trap (Figure 4(b)). Moreover, when we performed the measurements on the standard samples preliminarily kept for 12 h in the chamber under an argon atmosphere of 100 Pa, the emission intensities of H I 656.28 nm line increased compared with those measured within 1 h and were almost the same for all the samples, regardless of the hydrogen concentrations. This indicates that the water molecules in the argon gas cylinder and/or the gas line were adsorbed on the surface of the samples when allowing the argon gas to flow for 12 h. Therefore, the reduction in residual water molecules in the gas line (including the gas cylinder) by, e.g., heating the gas line and/or attaching more moisture traps is crucial to quantify ppm concentrations with our LIBS system. The necessity of the moisture trap and the removal of water molecules on samples for quantitative analysis of hydrogen *via* LIBS has been also reported in a previous study concerning hydrogen measurement for water rich magnesium sulfates epsomite.[18] In addition, the use of an atmospheric emission peak, such as carbon and oxygen, as standard could help the measurements

of hydrogen with ppm concentrations as a previous study reported.[18]

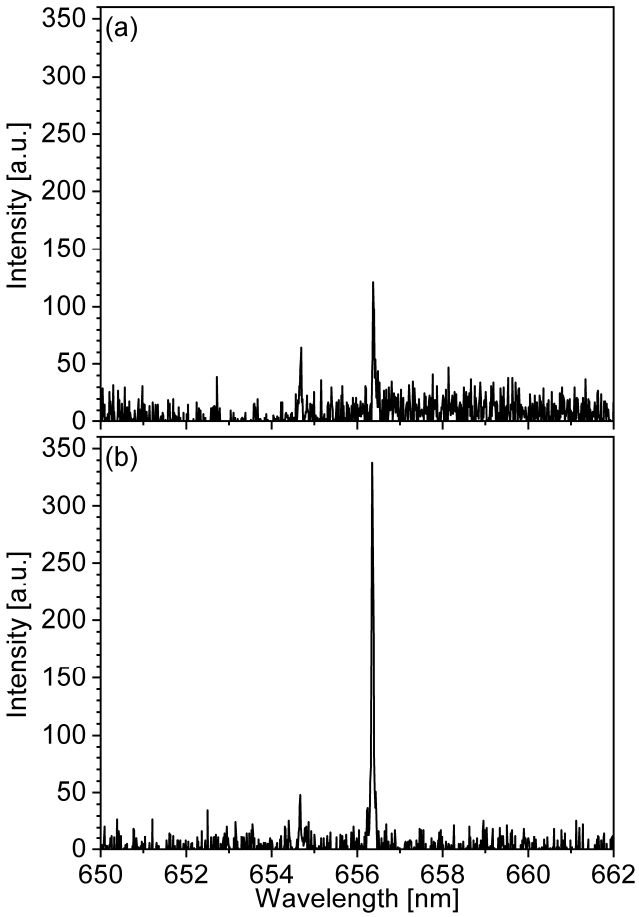

Figure 4. Laser-induced breakdown spectroscopy spectra of the standard sample with 0 mass% hydrogen measured under reduced helium (3000 Pa) (a) with and (b) without the moisture trap in the gas line.

3.2 Quantitative analysis

We used the calibration curve obtained under the reduced helium atmosphere (Figure 3) for the quantitative analysis of hydrogen in a typical hydrogen storage alloy, MgH_2. As for the previous experiment on the standard samples, analysis was based on the spectra obtained with the second shot of the pulsed laser. Table 3 compares the results obtained *via* LIBS and inert gas fusion/gas chromatography for samples that were preliminarily heated at 350 °C in an argon atmosphere for different times. The hydrogen concentrations obtained *via* LIBS decreased with the increase in the heating time, due to the following reaction, suggested in a previous report:[40]

$$MgH_2 \rightarrow Mg + H_2 \qquad (3).$$

Although the hydrogen concentration in the sample heated for 6 h was below the LOQ of our LIBS system, the results obtained with the propose method were in good agreement with those determined *via* inert gas fusion/gas chromatography. These results confirm the applicability of LIBS for the quantitative evaluation of different hydrogen concentrations in MgH_2. Each measurement lasts only a few seconds, whereas the inert gas fusion/gas chromatography analysis takes several minutes. Therefore, the proposed LIBS-based method can rapidly estimate hydrogen concentrations below 7.6 mass%, even after including the calibration time for standard samples. To the best of our knowledge, this is the first study to demonstrate the potentiality of LIBS for the quantitative analysis of hydrogen at concentrations above 5.7 mass%. Besides, a spatial resolution of a few hundred micrometers in plane and dozens of micrometers in depth per laser shot can be attained using a LIBS apparatus equipped with a laser scanning system, which was confirmed for lithium-ion battery cathode and carbon sheet in our previous studies.[23,24] Therefore, future works should focus on the application of the present LIBS technique to the two- and three-dimensional hydrogen analysis of solid-state materials, such as fuel cells, metals that showed hydrogen embrittlement, hydrogen-permeable films, and nickel/metal hydride rechargeable batteries. As a

previous study reported, in this case, investigating the relationship between the hydrogen emission intensity and sample geometry is also important.[19]

Table 3. Intensity of hydrogen emission line (H I 656.28 nm line) *via* laser-induced breakdown spectroscopy spectra from actual MgH_2 samples heated at 350 °C for different times under argon flow and the derived hydrogen concentration, alone with the hydrogen content estimated *via* inert gas fusion/gas chromatography. Each emission intensity value reported in the table is the average of 10 values. The errors represent one standard deviation.

	LIBS		Inert gas fusion/gas chromatography
Heating time [h]	Intensity [a.u.]	Hydrogen concentration [mass%]	Hydrogen concentration [mass%]
2	5727 ± 130	7.3 ± 0.2	7.62 ± 0.05
3	5547 ± 289	7.1 ± 0.4	7.73 ± 0.04
4	1786 ± 261	2.0 ± 0.4	2.62 ± 0.11
6	366 ± 121	0.1 ± 0.2	0.43 ± 0.02

4. CONCLUSIONS

We developed a method to quantify hydrogen concentrations in the 0.2–7.6 mass% range *via* LIBS under a 3000 Pa helium atmosphere. The measurement time for a single sample is a few seconds. A straight-line calibration curve was acquired by measuring the hydrogen emission intensity (at 656.28 nm) for standard Mg/MgH_2 mixtures containing 0, 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 7.6 mass% of hydrogen. The residual water molecules in the samples and the LIBS gas line were removed using a desiccator containing silica gel and using a moisture trap, respectively. Then, the hydrogen concentrations of actual MgH_2 samples heated at 350 °C for 2, 3, 4, and 6 h in an argon atmosphere were estimated *via* the proposed method, and the results were consistent with those obtained through inert gas fusion/gas chromatography. We also explained why the emission intensity measured at 656.28 nm under a reduced argon atmosphere was lower than that under a reduced helium based on the energy levels of the argon and helium metastable states. Our results indicate the feasibility of rapid quantitative analysis of hydrogen in MgH_2 *via* LIBS; furthermore, the LIBS technique is applicable also to two- and three-dimensional analyses.

Acknowledgments

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